

Magnetic/Conducting Hybrid Compound Composed of 1-D Chain $[\text{Mn}_2\text{Cl}_5(\text{EtOH})]_{\infty}^{-}$ and BEDT-TTF Stacking Layer

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An assembled compound $(\text{BEDT-TTF})_2[\text{Mn}_2\text{Cl}_5(\text{EtOH})]_{\infty}^{-}$ (1) consisting of two structural lattices of Mn(II)–Cl one-dimensional (1-D) chains and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) stacking layers was synthesized by electrochemical crystallization. Compound 1 crystallized in triclinic space group *P*-1 (#2) with $a = 13.1628(5)$ Å, $b = 20.3985(9)$ Å, $c = 7.4966(3)$ Å, $\alpha = 98.3498(8)^\circ$, $\beta = 104.980(1)^\circ$, $\gamma = 74.602(2)^\circ$, $V = 1868.3(1)$ Å³, and $Z = 2$. The 1-D chains and the stacking layers are aligned along the *c*-axis of the unit cell. The 1-D chain is described as $[\text{Mn}_2\text{Cl}_5(\text{EtOH})]_{\infty}^{-}$ in which two Mn(II) ions and four Cl[−] ions form a ladder-like chain with Kagomé (cuboidal) sublattices, and the remaining Cl[−] ion and an ethanol molecule cap the edge-positioned Mn(II) ions of the chains. The BEDT-TTF molecules are packed between the Mn–Cl chains (*ac*-plane), the intermolecular S...S contacts of which are approximately found in the range 3.440(2)–3.599(2) Å. The packing feature of BEDT-TTF molecules is very similar to that of $(\text{BEDT-TTF})_2\text{ClO}_4(\text{TCE})_{0.5}$ (TCE = 1,1,2-trichloroethane) (*J. Am. Chem. Soc.*, **105**, 297 (1983)). Regarding the electronic state of each BEDT-TTF molecule, Raman spectroscopic analysis and ESR study revealed the presence of half-valence BEDT-TTF molecules (charge delocalization) in 1. Magnetic measurements clearly demonstrated that the paramagnetic spins on the 1-D chain $[\text{Mn}_2\text{Cl}_5(\text{EtOH})]_{\infty}^{-}$ arrange antiferromagnetically in the low-temperature region. Additionally, 1 exhibits metallic conductivity in the temperature range 2.0–300 K ($\sigma = 21$ S cm^{−1} at 300 K and 1719 S cm^{−1} at 2.0 K), due to the contribution of the stacked BEDT-TTFs. Consequently, these peculiarities that correspond to antiferromagnetic/metallic conductivity demonstrate the “bi-functionality” of 1. © 2002 Elsevier Science (USA)

INTRODUCTION

In the last decade, the field of molecule-based functional materials has made significant progress, especially for bulk magnetic materials (1–7) and highly conducting materials (8–10). For molecule-based magnetic materials, multi-dimensional lattices, which allow the magnetic arrangement of individual magnetic spins in the long-range order, are well designed by choosing adequate molecular blocks (and/or metal ions) and bridging ligands to form sublattices and counter ions to fill the voids among multi-dimensional lattices. Several attractive materials are available such as a series of heterometal assemblies with oxalate ($\text{C}_2\text{O}_4^{2-}$) linkage formulated as $A^+[M^{\text{II}}M^{\text{III}}(\text{C}_2\text{O}_4)_3]^-$ (A^+ = monocation) (5) and Prussian-blue-type compounds using combinations of $[M^{\text{III}}(\text{CN})_6]^{3-}$ ($M = \text{Fe}, \text{Mn}, \text{Cr}$) and metal-complexes possessing a coordination-acceptor character such as Ni(II) polyamine complexes (6) and Mn(III) salen analogues (7). On the other hand, the fabrication of molecule-based highly conducting materials was promoted by the development of organic charge-transfer molecules with tetrathiafulvalene (TTF) derivatives (8–10). For the fabrication of these materials, synthetic chemists have realized that the control of molecular arrangement in three-dimensional (3-D) sphere is very important for deriving bulk physical properties. Based on these synthetic backgrounds, recent challenges have been directed at fabricating molecule-based functional materials with “bi-functionality”, one target of which is the magnetic/conducting hybrid material. Thus, an effective strategy for fabricating such materials is to combine magnetic multi-dimensional lattices and organic conducting columns or layers (Chart 1). Recently,

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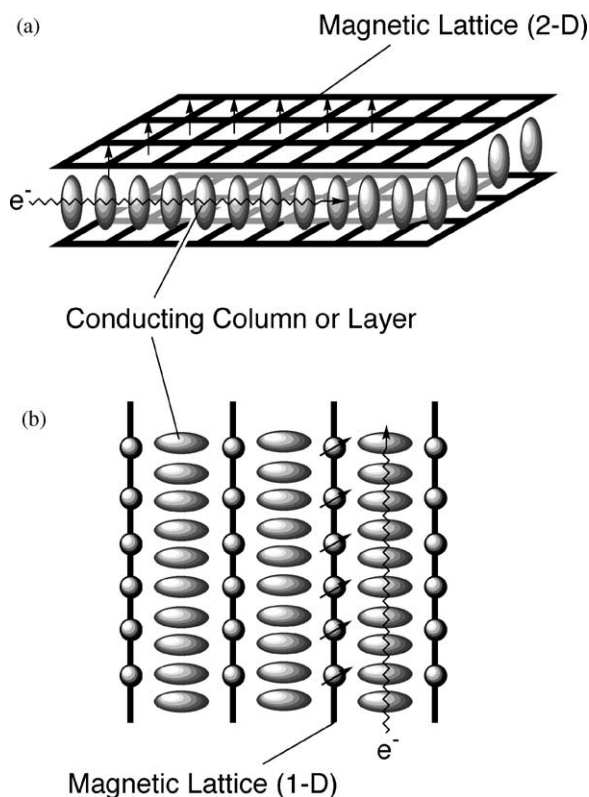


CHART 1.

Coronado *et al.* succeeded in synthesizing the first bi-functional compound (ferromagnetism and metallic conductivity), which was composed of ferromagnetic 2-D (coordination-lattice) layers of $[\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)_3]^-$ and conducting layers of bis(ethylenedithio)tetrathiafulvalene ($\text{BEDT-TTF})^{\text{n}+}$ (a candidate for the material of Chart 1a) (11). Although organic conducting systems with discrete metal-complexes are well known (12), hybrid systems in which both magnetic multi-dimensional lattices and organic conducting columns coexist are very rare, with only the Coronado *et al.* compound being known to date. We present herein a new hybrid system, $(\text{BEDT-TTF})_2[\text{Mn}_2\text{Cl}_5(\text{EtOH})]$ (**1**), which is composed of anti-ferromagnetic 1-D chains of $[\text{Mn}_2\text{Cl}_5(\text{EtOH})]^-$ and BEDT-TTF conducting layers (a candidate for the material of Chart 1b).

EXPERIMENTAL SECTION

General Procedures and Materials

Electrochemical crystallization was carried out under nitrogen atmosphere. All chemicals used for the syntheses were of reagent grade. BEDT-TTF was prepared according to the method described by Larsen and Lenoir, and

recrystallized from CHCl_3 (13). Solvents used in the syntheses were dried by refluxing over common drying agents and freshly distilled under nitrogen atmosphere before use.

Preparation of $(\text{BEDT-TTF})_2[\text{Mn}_2\text{Cl}_5(\text{EtOH})]$ (**1**)

Electrochemical crystallization was carried out at a current of $0.1 \mu\text{A}$ for more than 1 week using an H-shaped cell in which each electrode space was separated by a glass-filter. Each cell contained 100 mL of 1,2-dichloromethane-EtOH (9:1) mixture saturating BEDT-TTF with $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (75 mg). Thin plate-like crystals adhering to the anode were obtained. Anal. Calcd. for $(\text{BEDT-TTF})_2\text{Mn}_2\text{Cl}_5(\text{EtOH})$: $\text{C}_{22}\text{H}_{22}\text{S}_{16}\text{Mn}_2\text{Cl}_5\text{O}$: C, 23.97; H, 2.01. Found: C, 23.29; H, 2.09.

Physical Measurements

Magnetic susceptibility data were obtained over the temperature range 2.0–300 K at 1 T using an MPMS5 SQUID susceptometer (Quantum Design, Inc.). Corrections were made for diamagnetism using Pascal's constants (14) and for sample holders. Four-probe ac resistance measurements were conducted on a single crystal with current flow along the *c*-axis of the single-crystal unit cell using a Quantum Design PPMS. Measurement temperature was scanned in the range 2.0–300 K. Electrical contacts to the crystal were made with $20 \mu\text{m}$ gold wire and carbon paste. X-band electron spin resonance spectra (ESR) of a polycrystalline sample were measured at room temperature with a JEOL JEX-FE3X operating at 9.85 GHz and 1 mW power. Single-crystal Raman spectra were measured at ambient conditions using a Renishaw Raman grating microscope spectrometer equipped with an He-Ne laser ($\lambda = 632.6 \text{ nm}$) in 180° reflective geometry. To avoid damage, the laser power was attenuated to as low as $170 \mu\text{W}$ and focused in a $5 \mu\text{m}$ spot onto the sample surface. Spectra were collected in the static mode in the $1200\text{--}1700 \text{ cm}^{-1}$ range for 1000 s with 2 cm^{-1} resolution.

X-Ray Data Collection, Reduction, and Structural Determination

Single-crystal X-ray crystallographic measurement of **1** was conducted on a Rigaku imaging plate diffractometer (RAXIS-RAPID) with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The crystal dimensions are $0.18 \times 0.13 \times 0.03 \text{ mm}^3$. 17,345 reflections were collected at $-100 \pm 1^\circ\text{C}$ and 8409 reflections were found to be unique ($R_{\text{int}} = 0.041$). The structure was elucidated by direct methods (SIR92) (15) and expanded using Fourier techniques (16). Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced as fixed

TABLE 1
Crystal Data for (BEDT-TTF)₂[Mn₂Cl₅(EtOH)] (1)

| | |
|--------------------------------------------------|-----------------------------------------------------------------------------------|
| Formula | C ₂₂ H ₂₂ S ₁₆ Mn ₂ Cl ₅ O |
| Formula weight | 1102.52 |
| Crystal system | Triclinic |
| Space group | <i>P</i> -1 (#2) |
| <i>a</i> (Å) | 13.1628(5) |
| <i>b</i> (Å) | 20.3985(9) |
| <i>c</i> (Å) | 7.4966(3) |
| α (°) | 98.3498(8) |
| β (°) | 104.980(1) |
| γ (°) | 74.602(2) |
| <i>V</i> (Å ³) | 1868.3(1) |
| <i>D</i> _{calcd.} (g cm ⁻³) | 1.960 |
| <i>T</i> (K) | 173 |
| <i>Z</i> | 2 |
| μ (MoK α) (cm ⁻¹) | 19.52 |
| <i>F</i> (000) | 1106.00 |
| No. of reflections | 17345 |
| Unique reflections | 8409 (<i>R</i> _{int} = 0.041) |
| Observed reflections | 4651 (<i>I</i> < 3.00 σ (<i>I</i>)) |
| GOF | 0.93 |
| <i>R</i> 1 | 0.032 |
| <i>R</i> 2 | 0.047 |
| <i>R</i> w | 0.074 |

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, R2 = \frac{\sum (F_o^2 - F_c^2)}{\sum F_o^2}, \text{ and } Rw = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{I} (I > 3.00\sigma(I))$$

contributors. Full-matrix least-squares refinements based on 4651 observed reflections (*I* > 3.00 σ (*I*)) were employed (unweighted and weighted agreement factors of *R*1 = $\frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, *R*2 = $\frac{\sum (F_o^2 - F_c^2)}{\sum F_o^2}$, and *R*w = $\frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{I}$ (*I* > 3.00 σ (*I*)) were used). All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (17). Crystallographic data and details of the structural determination of **1** are summarized in Table 1.

RESULTS AND DISCUSSION

Structural Descriptions

Well-defined crystals of **1** were prepared by electrochemical crystallization in 1,2-dichloromethane-EtOH mixed solvent (9:1) containing BEDT-TTF and MnCl₂·4H₂O. Compound **1** crystallizes in the triclinic space group *P*-1 (*Z* = 2). ORTEP representation of a formula unit of **1** is depicted in Fig. 1a. Selected bond distances and angles are listed in Table 2. The structure of **1** comprises two parts: the magnetic [Mn₂Cl₅(EtOH)]_∞⁻ 1-D chains aligned along the *c*-axis of the unit cell and the conducting BEDT-TTF layers stacked parallel to the magnetic 1-D chains, as shown in Fig. 2. For the [Mn₂Cl₅(EtOH)]_∞⁻ chain depicted in Fig. 3, two Mn^{II} ions and four chloride ions form a Kagomé-like (cuboidal)

sublattice with an average Mn–Cl bond distance of 2.572(1) Å. The ethanol molecule and the remaining chloride ion cap the edge-positioned Mn^{II} ions with bond distances of Mn–O_{EtOH} = 2.189(3) Å and Mn–Cl₅ = 2.464(1) Å to form a 1-D ladder-like chain continuing mono-Kagomé (cuboidal) units. To date, several Cl-bridged Mn(II) 1-D chain compounds have been reported, which consist mainly of μ_2 -Cl or di- μ_2 -Cl alternating single chains (18,19). Among them, only the 1-D chain compound [MnCl₂(THF)_{1.6}], reported by Sobota *et al.* contains a double-cuboidal fragment in the chain, similar to the Kagomé-like (cuboidal) sublattice of **1** (20). The ladder-like 1-D chain system observed in **1** may be the first example in the category of halogen-bridged metal complexes. Previous data of the geometry around Mn ions suggest that both Mn1 and Mn2 in **1** are di-valent. It is surmised that two asymmetric BEDT-TTF molecules comprise one formula unit. The central C=C bond (C5–C6 and C15–C16) distances in both molecules found to be 1.372(5) Å, and the external/ring C=C bond (C3–C4, C7–C8, C13–C14, and C17–C18) distances are in the range 1.349(6)–1.363(6) Å. The BEDT-TTF molecules are packed in the BEDT-TTF/ClO₄-type arrangement observed previously in (BEDT-TTF)₂ClO₄(TCE)_{0.5} (TCE = 1,1,2-trichloroethane) (Fig. 4) (21). The intermolecular S...S contacts are approximately found in the range 3.440(2)–3.599(2) Å. Consequently, the construction of the inorganic/organic hybrid lattice is achieved. As expected from the formula unit, the set of two BEDT-TTF molecules is monovalent, i.e., (BEDT-TTF)₂⁺ (vide infra).

Raman Spectroscopy

In many cases including charge-transfer salts with BEDT-TTF molecules, the definition of charge distribution is very difficult in cationic molecules (BEDT-TTF) and even in anionic fragments, which are sometimes presented as transition-metal complexes. In some situations, X-ray crystallographic data give us ambiguity in this point. Therefore, in order to clarify the correction of the charges on the BEDT-TTF molecules, Raman spectra of the single crystal of **1** were measured at room temperature. As shown in Fig. 5, characteristic spectra were obtained by an incidence on the surface parallel to the *b*-axis of the single-crystal unit cell. The two symmetrical (Raman active) C=C stretching modes, where the two C=C bonds are defined as central and external/ring, respectively, and are expected to be observed between 1400 and 1550 cm⁻¹, are particularly sensitive to the redox state of the donor molecule (22). The stretching vibrations of the central C=C (ν_3) and external/ring C=C (ν_4) bonds of the BEDT-TTF molecules were observed at 1485(2) and 1472(2) cm⁻¹, respectively. Thus, the correlation between the Raman frequencies of the C=C double bonds in

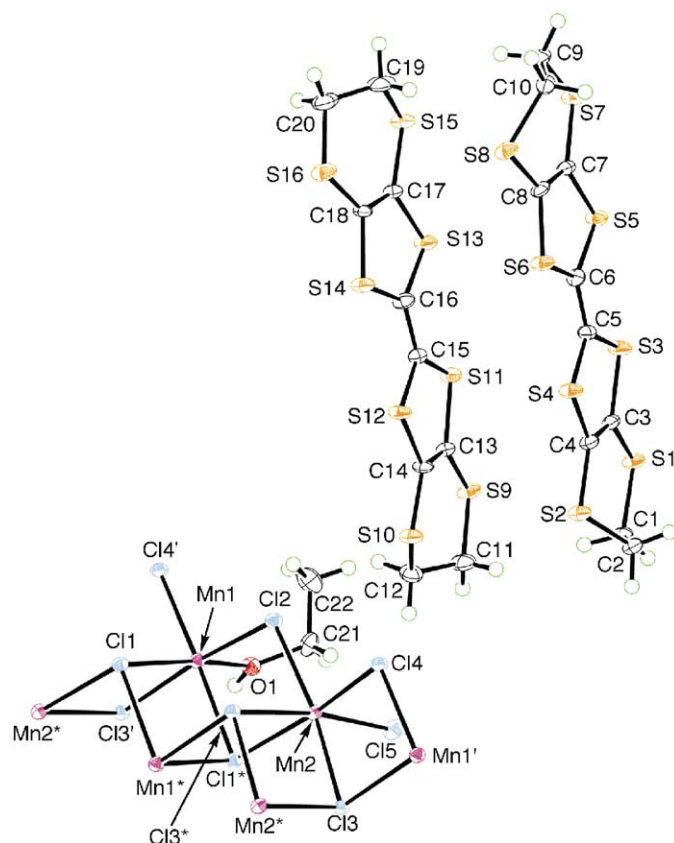


FIG. 1. ORTEP drawing of the formula unit and neighboring bonding atoms of 1 with the atom numbering scheme (50% probability thermal ellipsoids).

TABLE 2
Selected Bond Lengths (•) and Angles (deg) for (BEDT-TTF)₂[Mn₂Cl₅(EtOH)] (1)

| | | | |
|--------------------------|----------|----------------------------------------------|----------|
| S(3)–C(3) | 1.750(3) | S(13)–C(16) | 1.745(4) |
| S(3)–C(5) | 1.738(4) | S(13)–C(17) | 1.747(4) |
| S(4)–C(4) | 1.747(4) | S(14)–C(16) | 1.731(4) |
| S(4)–C(5) | 1.746(4) | S(14)–C(18) | 1.755(3) |
| S(5)–C(6) | 1.743(4) | C(13)–C(14) | 1.363(5) |
| S(5)–C(7) | 1.758(4) | C(15)–C(16) | 1.372(5) |
| S(6)–C(6) | 1.738(4) | C(17)–C(18) | 1.353(5) |
| S(6)–C(8) | 1.752(3) | Mn(2)–Cl(1) ^a | 2.632(1) |
| C(3)–C(4) | 1.361(5) | Mn(2)–Cl(2) | 2.519(1) |
| C(5)–C(6) | 1.372(5) | Mn(2)–Cl(3) | 2.586(1) |
| C(7)–C(8) | 1.349(5) | Mn(2)–Cl(3) ^b | 2.659(1) |
| Mn(1)–Cl(1) | 2.575(1) | Mn(2)–Cl(4) | 2.539(1) |
| Mn(1)–Cl(1) ^a | 2.623(1) | Mn(2)–Cl(5) | 2.464(1) |
| Mn(1)–Cl(2) | 2.481(1) | Mn(1)–Cl(1)–Mn(1) ^a | 92.16(4) |
| Mn(1)–Cl(3) ^c | 2.607(1) | Mn(1)–Cl(1)–Mn(2) ^a | 97.22(4) |
| Mn(1)–Cl(4) ^c | 2.498(1) | Mn(1) ^a –Cl(1)–Mn(2) ^a | 92.62(3) |
| Mn(1)–O(1) | 2.189(3) | Mn(1)–Cl(2)–Mn(2) | 98.92(4) |
| S(11)–C(13) | 1.744(4) | Mn(1) ^d –Cl(3)–Mn(2) | 91.39(3) |
| S(11)–C(15) | 1.742(4) | Mn(1) ^d –Cl(3)–Mn(2) ^b | 95.77(4) |
| S(12)–C(14) | 1.752(4) | Mn(2)–Cl(3)–Mn(2) ^b | 98.03(4) |
| S(12)–C(15) | 1.748(4) | Mn(1) ^d –Cl(4)–Mn(2) | 95.09(4) |

Symmetry operations: ^a $-x+3, -y, -z+3$.

^b $-x+3, -y, -z+2$.

^c $x, y, z+1$.

^d $x, y, z+1$.

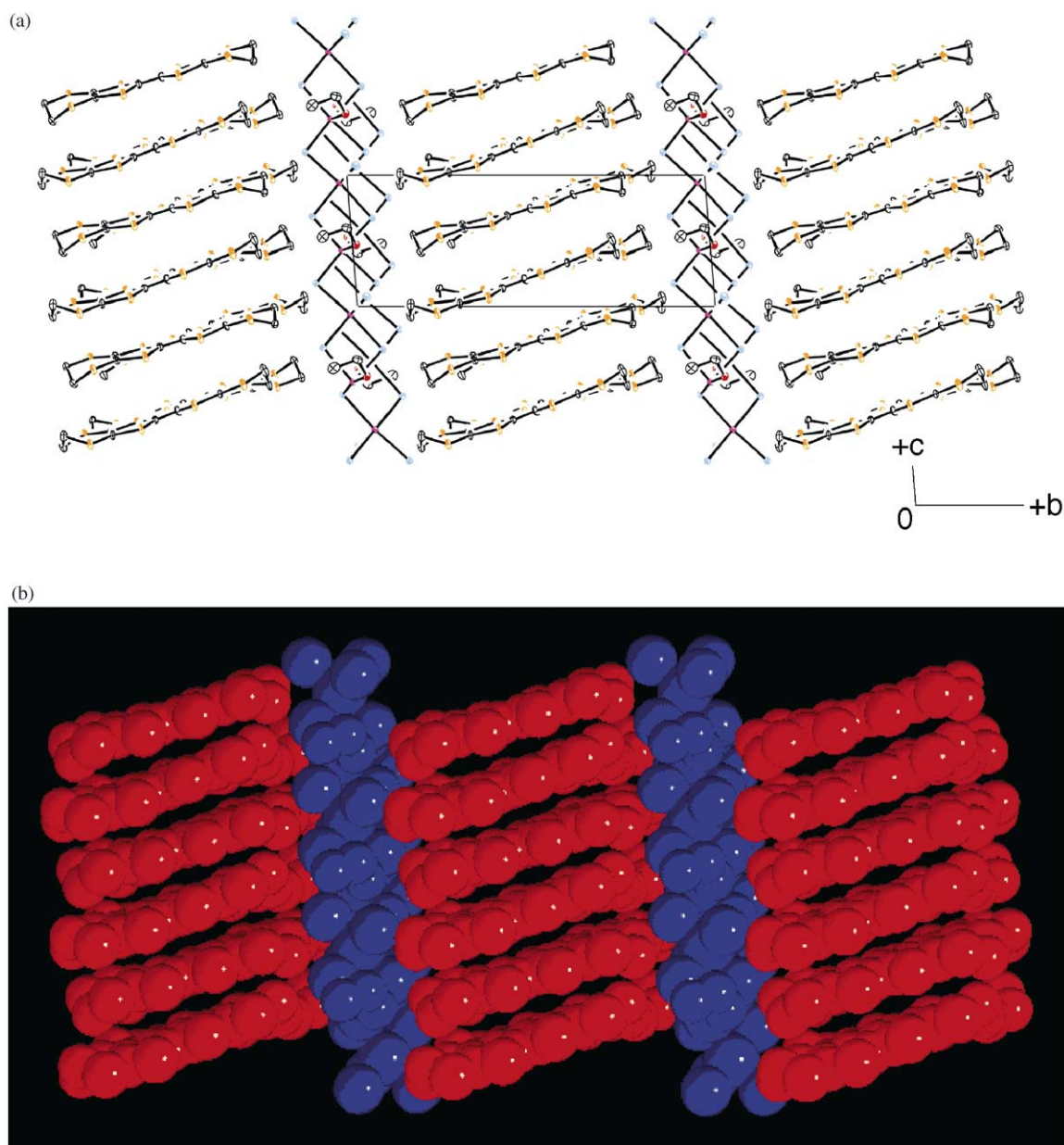


FIG. 2. Packing diagram projected along a -axis with a space-filling representation (b), where blue representation indicates the Mn-Cl chains and red one indicates the BEDT-TTF layers.

BEDT-TTF molecules and the degree of charge transfer (Z) was studied based on various BEDT-TTF salts synthesized thus far, giving the following equation (23, 24):

$$Z = w_3 \frac{1539 - v_3}{86.0} + w_4 \frac{1508 - v_4}{88.4},$$

where w_3 and w_4 are suitably normalized ($w_3 + w_4 = 1.0$) weighting factors. The estimation of **1** gave the degree of charge transfer on the BEDT-TTF molecule of 0.513 with $w_3 = w_4 = 0.5$. This result is consistent with expectations

based on structural aspects, which are attributed to the fact that the central C=C bonds on the BEDT-TTF molecule are found to be ca. 1.37 Å, being the typical value of the half-charged BEDT-TTF (25). The half-charge distribution of BEDT-TTF molecules, namely, the charge delocalized state, supports indirectly the metallic conducting property of **1** over the temperature range 2–300 K (see the Electrical conducting properties section), and leads us to suppose a contribution of Pauli-like paramagnetism in the magnetic data rather than an explanation employing the local radical spin of the magnetic moment $S = \frac{1}{2}$ caused by the

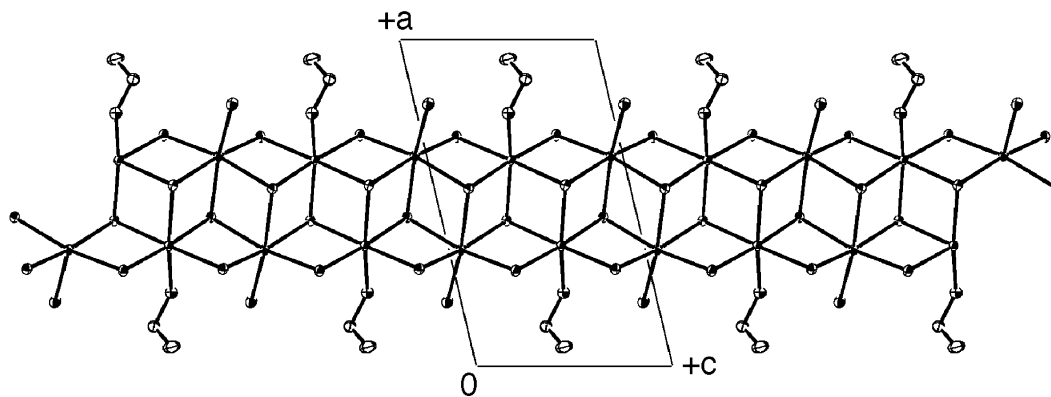


FIG. 3. View of the 1-D chain $[\text{Mn}_2\text{Cl}_5(\text{EtOH})]^-$ with the Kagomé sublattices. The chain runs along c -axis of the unit cell.

$(\text{BEDT-TTF})_2^+$ molecule in addition to the large magnetic moments from the two $\text{Mn}(\text{II})$ ions (vide infra).

Magnetic Properties

The temperature dependence of the magnetic susceptibility of the polycrystalline sample of **1** was measured in the temperature range 2.0–300 K. The temperature dependence of χ_m and $\chi_m T$ is given in Fig. 6. Upon cooling, the $\chi_m T$ value of $9.20 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K decreases slightly and linearly until approximately 30 K, and then decreases abruptly to $1.98 \text{ cm}^3 \text{ K mol}^{-1}$ at 2.0 K. Although the Curie paramagnetic approximation in the high-temperature region with $C = 9.2(1) \text{ cm}^3 \text{ K mol}^{-1}$ may be comparable to

$9.13 \text{ cm}^3 \text{ K mol}^{-1}$ calculated by assuming a set of local spins, two $S = \frac{5}{2}$ arising from two $\text{Mn}(\text{II})$ ions and one $S = \frac{1}{2}$ arising from BEDT-TTF molecules ($g = 2.00$), the slightly large $\chi_m T$ value at 300 K and the linear decrease of $\chi_m T$ in the high-temperature region could be due to the contribution of Pauli-like paramagnetism. X-band ESR measurement at room temperature confirmed the coexistence of the isolated radical spins and $\text{Mn}(\text{II})$ ions with a sharp signal of $g = 2.001$ and a broad signal around $g = 2$, respectively (Fig. 7). The decrease of $\chi_m T$, especially in the low-temperature region, clearly indicates that the intra-chain antiferromagnetic interaction is operative between $\text{Mn}(\text{II})$ ions via μ_2 - and μ_3 -chloride ions, being an antiferromagnetic chain. A previous work estimated the magnetic

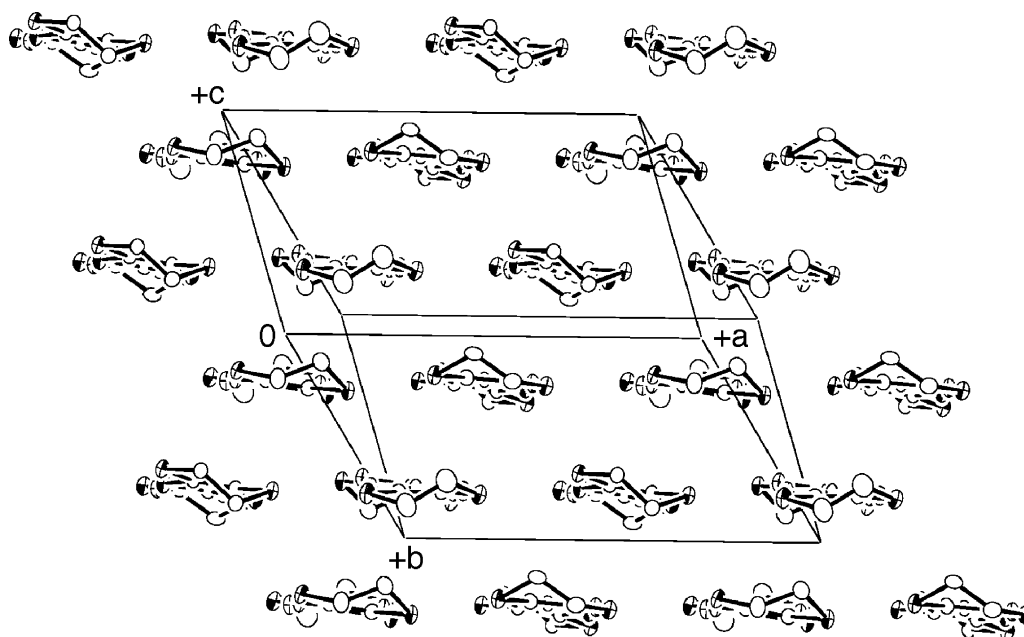


FIG. 4. View of the BEDT-TTF layer, which is formed along ac -plane defined as the unit cell.

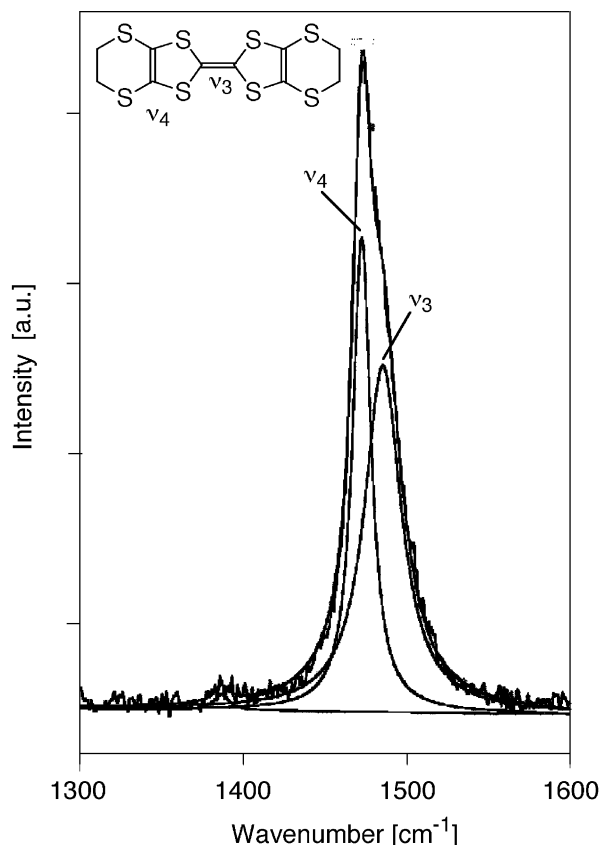


FIG. 5. Raman spectra of **1** measured on a single crystal (red line), where the blue line corresponds to smoothing line of the observed spectral data. The individual contribution of the central C=C (ν_3) and the external/ring C=C (ν_4) bonds of the BEDT-TTF molecules is isolated by a least-squares calculation as 1485(2) and 1472(2) cm^{-1} , respectively.

exchange coupling between Mn(II) ions via di- μ_2 -Cl to be $J/k_B = -0.59$ and -0.69 K, based on compounds $\text{MnCl}_2(\text{Py})$ and PyHMnCl_3 , respectively (26). Therefore, the

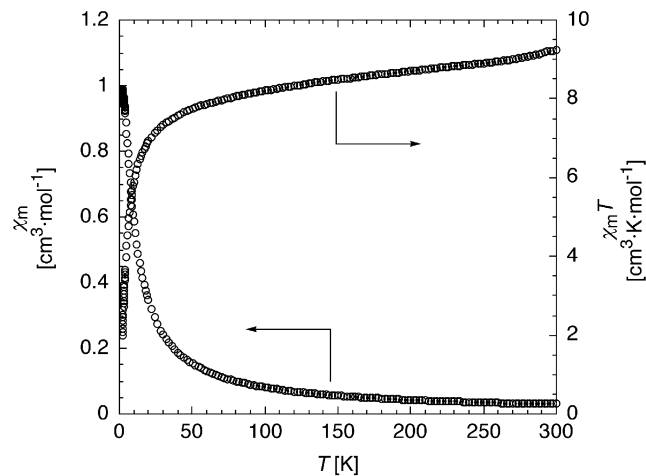


FIG. 6. Temperature dependences of χ_m and $\chi_m T$ for **1** measured in the temperature range 2.0–300 K.

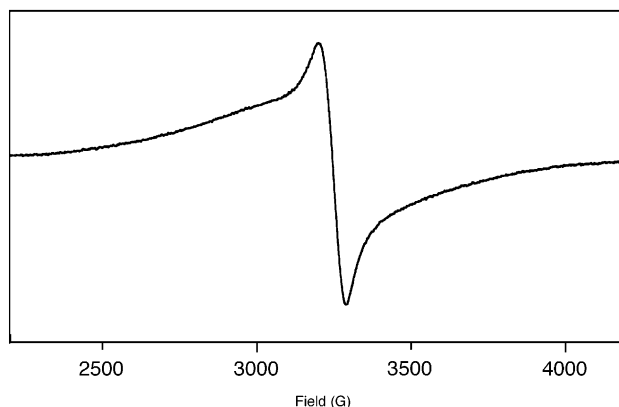


FIG. 7. ESR spectrum of powder samples of **1** measured at room temperature (microwave frequency 9.85 GHz, power 1 mW).

exchange coupling seems weak in **1**, similar to the above compounds (no antiferromagnetic ordering). Thus, as known in general, the Kagomé lattices allow spin frustration in antiferromagnetic coupling between neighboring magnetic centers, but in this system, weak exchange coupling in the Kagomé sublattice is not expected to have much influence of spin frustration on magnetism of **1**.

Electrical Conducting Properties

The most appealing feature of **1** is its electrical conducting property. The electrical conductivity of a single crystal of **1** was measured in the temperature range 2.0–300 K as shown in Fig. 8, where the electrical contacts were attached parallel to the conducting layers (along the c -axis of the unit cell). The temperature dependence of the electrical conductivity revealed that this material exhibited

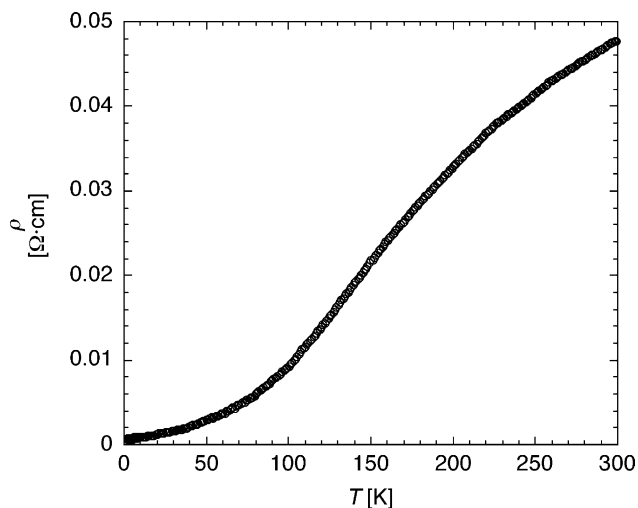


FIG. 8. Temperature dependence of resistance of **1** measured in the temperature range 2.0–300 K.

a metallic behavior in the temperature range 2.0–300 K with $\sigma = 21 \text{ S cm}^{-1}$ at 300 K and 1719 S cm^{-1} at 2.0 K. The resistivity decreases to exhibit a concave curvature as the temperature is decreased, without any signs of metal–insulator (M–I) transition, even at 2 K. The residual resistivity ratio (RRR) is estimated as $RRR = \rho_{2\text{K}}/\rho_{\text{r.t.}} = 0.0163$. The small RRR value proves that there is a weak contribution from the impurity scattering in the transport. The structural aspects of the BEDT-TTF arrangement convinced us sufficiently to be its conducting behavior.

CONCLUSIONS

The present compound is a hybrid material in which magnetic one-dimensional lattices and conducting layers coexist in a crystal packing, and is considered to be a unique inorganic/organic material with antiferromagnetic/metallic conductivity. Investigations are under way to understand the correlation between bi-functionalities, for example, resistivity measurements under an external field and under pressure. For the fabrication of such bi-functional materials, the control of molecular arrangement is the key, especially for producing satisfactory conducting energy bands. A combination of well-designed magnetic lattices (1-D, 2-D, and 3-D bonding lattices), which should be constructed unequivocally in assembly reactions, and organic conducting molecules such as TTF derivatives, is expected to create other unique bi-functional materials, including ferromagnetic/superconducting materials.

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